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YELLOW ANIONIC DISAZO DYES

The present invention relates to novel yellow anionic dyes, a process for their preparation, certain novel intermediates necessary for their preparation and the use of these dyes for dyeing natural or synthetic materials, in particular, paper.

The use of diaminobenzanilides as building blocks for the synthesis of bisazo dyes and the advantages thereof has been described in Dyes and Pigments, 17, 297-302 (1991). On this basis, a number of bisazo orange and yellow dyes containing pyrazolones and phenolic derivatives as coupling components have been described, for example, in DE 818,669, DE 845,084, DE 2,362,995, GB 28,569, US 2,228,321 and in JP 51-11817, whilst further symmetrical bisazo dyes containining 1-phenyl-5-amino pyrazoles have also been reported in US 5,545,725, whilst US 2,544,087 discloses certain bis-acetoacetanilide derivatives.

However, a requirement exists to provide further anionic dyes especially of neutral or greenish yellow shades, which dyes exhibit excellent degrees of exhaustion with high colour strength, whilst being sufficiently water-soluble to provide stable aqueous formulations without the need for large quantities of solubilizers. Furthermore, dyings obtained should exhibit high degrees of bleed- and light-fastness, be even- or top-sided and be readily bleachable.

Surprisingly, it has now been found that certain bisazo dyes based on diaminobenzanilides exhibit excellent effects with respect to the desired properties.

Accordingly, the invention relates to compounds of the formula

$$A_{1}-N, \qquad \qquad H_{3a}$$

$$A_{1}-N, \qquad \qquad H_{2}$$

$$N-A_{2}$$

$$R_{1}$$

$$N-A_{2}$$

$$R_{1}$$

$$N$$

in which

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 R_1 represents hydrogen, substituted or unsubstituted C_1 - C_8 alkyl, substituted or unsubstituted C_1 - C_8 alkoxy or SO_3H ,

R₂ represents SO₃H or CO₂H,

 R_3 and R_{3a} each, independently of the other, represent hydrogen, a C_1 - C_4 alkyl group, which may be substituted or unsubstituted, halogen, hydroxy, substituted or unsubstituted C_1 - C_4 alkoxy, carboxy, NH $_2$ or NHC $_1$ - C_4 alkyl and each of the residues

 A_1 and A_2 , independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

 X_1 represents C_1 - C_4 alkyl, or phenyl which is unsubstituted or monosubstituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen and

X₂ represents phenyl which is unsubstituted, mono-, di- or trisubstituted by one or two SO₃H, SO₂NHC₁-C₄ alkyl groups which alkyl groups may be substituted, SO₂C₁-C₄alkyl, C₁-C₄substituted or unsubstituted alkyl, hydroxy, C₁-C₄alkoxy, halogen, CF₃, NH₂, NHCOC₁-C₄alkyl, NHCOOC₁-C₄alkyl, NHCONHC₁-C₄alkyl, CO₂H, CONHC₁-C₄alkyl or NO₂; a 1- or 2-naphthyl residue which is unsubstituted or substituted by one or two SO₃H, SO₂NHC₁-C₄alkyl, carboxy, CONHC₁-C₄alkyl, carboxyC₁-C₄alkyl or carboxyaryl groups or a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated and be further substituted by C₁-C₄alkyl, C₁-C₄alkoxy or halogen and which may be attached to the NH-atom in formula (2) either via the hetero- or benzo-nucleus, in the case of benzannelated heterocycles;

a derivative of barbituric acid of the formula

in which

Y represents O, NCN or NCONH₂; a 2,4,6-triaminopyrimidine;

a pyridone derivative of the formula

$$Q_1$$
 Q_2
 Q_3
 Q_3
 Q_3
 Q_3

in which

 Q_1 represents hydrogen, hydroxy, C_1 - C_2 alkyl, hydroxyethyl, 2-(C_1 - C_2 alkoxy)alkyl, C_1 - C_2 alkoxy, COOH, CONH $_2$ or COO C_1 - C_2 alkyl,

Q₂ represents hydrogen, CN, CONH₂, halogen, SO₃H or C₁-C₂alkyl which is unsubstituted or substituted by hydroxy, phenyl or SO₃H,

 Q_3 represents hydrogen, phenyl, C_1 - C_2 alkylphenyl, cyclohexyl or C_1 - C_4 alkyl which is unsubstituted or substituted by hydroxy, CN, C_1 - C_2 alkoxy or SO_3 H and

Q₄ represents hydrogen or hydroxy;

an aminopyrazole or a pyrazolone derivative of formula

in which

 R_4 represents hydrogen, substituted or unsubstituted C_1 - C_4 alkyl, C_2 - C_4 alkenyl,NHCO C_1 - C_4 alkyl or CO_2H , each

 R_5 and R_6 , independently of the other, represent hydrogen, halogen, C_1 - C_4 alkyl, SO_3H or CO_2H and

 R_7 represents hydrogen or C_1 - C_4 alkyl;

a benzoic acid derivative of formula

$$R_7$$
 OH R_8 R_8 R_7 OH R_8 R_8 R_7 OH R_8 R

in which

 R_7 represents hydrogen or $C_1\text{-}C_4$ alkyl and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 and R_{10} , each one independently of the other, represent hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen, NH₂, NHCO C_1 - C_4 alkyl, NO₂, SO₃H, CO₂C₁- C_4 alkyl or CONHC₁- C_4 alkyl groups,

with the proviso that in compounds of formula

$$A_{1} = N_{1} + N_{2} + N_{3a} + N_{1} + N_{2} + N_{$$

if

 $R_{1},\,R_{2},\,R_{3}$ and R_{3a} each, independently of the others, are hydrogen or $SO_{3}H,$ then

 A_1 and A_2 are not both a 1-phenyl or 1-sulphophenyl-3-methyl-5-aminopyrazole residue, or, if

R₁, R₂, R₃ and R_{3a} represent hydrogen and

A₁ is a residue of formula (9) in which

R₇ represents hydrogen or methyl, then

A₂ does not represent a 1-phenyl or 1-sulphophenyl-3-methyl- or 3-carboxy pyrazol-5-one residue

or, if

 $R_{1},\ R_{3}$ and R_{3a} are hydrogen and R_{2} is $SO_{3}H$ and one of

 A_1 and A_2 represents a 1-sulphophenyl-3-methyl pyrazol-5-one residue, then the other is not a residue of formula (11) in which both

 R_9 and R_{10} are hydrogen, or if

A₁ represents a 1-nitrophenyl-, a 1-phenyl- or an unsubstituted 3-methyl pyrazol-5-one residue,

A2 is not a residue of formula (9) in which R7 represents hydrogen, or if

 $R_1,\ R_3$ and R_{3a} represent hydrogen, R_2 is CO_2H and

 A_1 represents a residue of formula (9), in which R_7 is hydrogen,

A₂ is not a residue of formula (2) or formula (7);

in compounds of the formula

if

 R_2 represents CO_2H , R_3 represents hydroxy or methoxy and R_{3a} represents hydrogen, A_1 and A_2 do not represent residues of formulae (2) or (7) and, in compounds of the formula

if

 R_2 represents SO₃H and R_3 and R_{3a} both represent hydrogen A_1 and A_2 are not both 2,4-dihydroxyphenyl.

In one preferred aspect of the invention, the compounds of formula (1), contain a total number of two, three or four SO_3H and/or CO_2H groups. These sulphonic and/or carboxylic acid groups may be represented either, as written, in the form of the free acid or in the salt form, SO_3M and/or CO_2M . M is preferably one equivalent of a colourless cation, typically lithium, sodium, potassium, ammonium or the protonated form of a C_4 - C_{12} trialkylamine, C_4 - C_{12} diamine, C_2 - C_{12} alkanolamine or of a polyglycol amine, conveniently, triethanolamine trisglycol ether, or mixtures of such cationic species.

M as a protonated C₄-C₁₂trialkylamine may, for example, be a protonated N-ethyldimethylamine, N,N-diethylmethylamine, tri-n-propylamine, tri-n-butylamine, tri-isobutylamine, and, preferably, triethylamine or triisopropylamine.

M as a protonated C_4 - C_{12} diamine may, for example, be ethylenediamine, or 1,3-diaminopropane, in which one or both nitrogen atoms are additionally substituted by one or two C_1 - C_4 alkyl radicals, preferably methyl or ethyl radicals. M is preferably an N,N-dialkyl-1,3-diaminopropane. Illustrative examples are: N-ethylethylenediamine or N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N-diethylethylenediamine, N,N-diethylethylenediamine, 3-dimethylamino-1-propylamine or 3-diethylamino-1-propylamine. M as a protonated C_2 - C_{12} alkanolamine may be the protonated form of a monoalkanolamine, dialkanolamine, monoalkanolamine, monoalkanolamine, monoalkanolamine, monoalkanolamine or trialkanolamine or a mixture of different protonated alkanolamines. Illustrative examples are: protonated 2-aminoethanol, bis(2-hydroxyethyl)amine, N-(2-hydroxyethyl)dimethylamine, N-(2-hydroxyethyl)diethylamine, N,N-bis(2-hydroxyethyl)ethylamine or tris(2-hydroxyethyl)-amine.

One further preferred class of compounds of formula (1) is that of the formula

$$A_1 - N_1 \qquad \qquad P_3 \qquad \qquad O \qquad \qquad P_2 \qquad \qquad P_3 \qquad \qquad P_4 \qquad \qquad P_4 \qquad \qquad P_5 \qquad \qquad P_6 \qquad \qquad$$

in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

R₃ represents hydrogen, a C₁-C₄alkyl group, halogen, hydroxy, C₁-C₄alkoxy, carboxy, NH₂ or NHC₁-C₄alkyl,

R_{3a} represents hydrogen or NH₂ and

A₁ and A₂ are as defined above.

More preferably, however, in the above compounds of formula (13),

R₃ and R_{3a} both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of

an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

a pyridone derivative of the formula

$$Q_1$$
 Q_2
 Q_4
 Q_3
 Q_3
 Q_3
 Q_4
 Q_3

Q₁ represents C₁-C₂alkyl,

 $\ensuremath{\text{Q}}_2$ represents CN, CONH2 or CH2SO3H,

Q₃ represents C₁-C₂alkyl and

Q₄ represents hydroxy;

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}alkyl,\,SO_{3}H$ or $CO_{2}H$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

R₉ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy, hydroxy, halogen or SO₃H and R₁₀ represents hydrogen.

Most preferred compounds of formula (13) are those in which R_1 represents hydrogen, C_1 - C_4 alkoxy, especially methoxy, or SO_3H , R_2 represents SO_3H or CO_2H ,

 R_3 and R_{3a} both represent hydrogen and the coupling component A_1 is derived from an acetoacetylated amine of formula (2), barbituric acid or cyanimino barbituric acid, a pyridone derivative of formula (4) in which Q_1 represents methyl, Q_2 is CN, CONH₂ or CH₂SO₃H, Q_3 is ethyl or methyl and Q_4 is hydroxy, a compound of formula (5) or (7) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO₃H and R_6 represents hydrogen, or from salicyclic acid and the coupling component A_2 is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X_1 preferably represents methyl and X_2 preferably represents phenyl, which is monosubstituted by SO₃H or trisubstituted by SO₃H, methyl and methoxy or A_2 is is derived from a pyridone derivative of formula (4) in which Q_1 represents methyl, Q_2 is CN, CONH₂ or CH₂SO₃H, Q_3 is ethyl and Q_4 is hydroxy or from an aminpyrazole of formula (5) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO₃H and R_6 represents hydrogen.

A second preferred class of compounds of formula (1) is that of the formula

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH₂ and

 A_1 and A_2 are as defined for formula (1) above.

More preferably, however, in the above compounds of formula (14)

 R_3 and R_{3a} both represent hydrogen and

 A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2)

in which

X₁ represents C₁-C₄alkyl, and

X₂ represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO₃H,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid:

2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}alkyl,\,SO_{3}H$ or $CO_{2}H$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

$$R_8$$
 OH OH (9) or R_8 OH (10), R_7

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

Most preferred compounds of formula (14) are those in which R_1 represents hydrogen, C_1 - C_4 alkoxy, especially methoxy, or SO_3H , R_2 represents SO_3H or CO_2H ,

 R_3 and R_{3a} both represent hydrogen and the coupling component A_1 is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid, 2,4,6-triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen or from salicyclic acid, methyl salicyclic acid, phenol or methyl phenol and the coupling component A_2 is is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X_1 preferably represents methyl and X_2 preferably represents phenyl, which is monosubstituted by SO_3H or, especially, trisubstituted by SO_3H , methyl and methoxy or A_2 is derived from an aminpyrazole of formula (5) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen.

A third preferred class of compounds of formula (1) is that of formula

$$A_{1}-N$$

$$R_{3a}$$

$$N$$

$$R_{1}$$

$$N=N$$

$$A_{2}$$

$$(15),$$

in which

R₁ represents hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or SO₃H,

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH₂ and

 A_1 and A_2 are as defined for formula (1) above.

More preferably, however, in the above compounds of formula (15)

 $R_{\rm 3}$ and $R_{\rm 3a}$ both represent hydrogen and

A₁ and A₂, each one independently of the other, is derived from a coupling component selected from the group consisting of an acetoacetylated amine of the formula

$$X_1$$
 X_2 X_2 (2) ,

X₁ represents C₁-C₄alkyl, and

 X_2 represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO_3H ,

C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy, halogen or CO₂H;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_{5} represents hydrogen, halogen, $C_{1}\text{-}C_{4}aikyI,\,SO_{3}H$ or $CO_{2}H$ and

R₆ represents hydrogen;

a benzoic acid derivative of formula

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

 A_1 and A_2 , each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

hydrogen.

 R_9 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

Most preferred compounds of formula (15) are those in which

 R_1 represents hydrogen or C_1 - C_4 alkoxy, especially hydrogen, R_2 represents SO₃H or CO₂H, especially SO₃H, R_3 and R_{3a} both represent hydrogen and the coupling component A_1 is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid, triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO₃H and R_6 represents hydrogen or from salicyclic acid, methyl salicyclic acid, phenol or methyl phenol and the coupling component A_2 is is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X_1 preferably represents methyl and X_2 preferably represents phenyl, which is monosubstituted by SO₃H or, especially, trisubstituted by SO₃H, methyl and methoxy or A_2 is derived from an aminpyrazole of formula (5) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO₃H and R_6 represents

A fourth preferred class of compounds of formula (1) is that of formula

 R_1 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or SO_3H ,

R₂ represents SO₃H or CO₂H,

 R_3 represents hydrogen, a C_1 - C_4 alkyl group, halogen, hydroxy, C_1 - C_4 alkoxy, carboxy, NH_2 or NHC_1 - C_4 alkyl,

R_{3a} represents hydrogen or NH₂ and

 A_1 and A_2 are as defined for formula (1) above.

More preferably, however, in the above compounds of formula (16),

 $R_{\rm 3}$ and $R_{\rm 3a}$ both represent hydrogen and

 A_1 and A_2 , each one independently of the other, is derived from a coupling component selected from the group consisting of

an acetoacetylated amine of the formula

$$X_1$$
 X_2 (2) ,

in which

X₁ represents C₁-C₄alkyl, and

 X_2 represents phenyl, which is unsubstituted, mono-, di- or trisubstituted by SO_3H ,

 C_1 - C_4 alkyl, hydroxy, C_1 - C_4 alkoxy, halogen or CO_2H ;

barbituric acid or cyanoiminobarbituric acid;

2,4,6-triaminopyrimidine;

citrazinic acid;

an aminopyrazole or a pyrazolone derivative of formula

in which

R₄ represents C₁-C₄alkyl or CO₂H,

 R_5 represents hydrogen, halogen, $C_1\text{--}C_4alkyl,\,SO_3H$ or CO_2H and

R₆ represents hydrogen:

a benzoic acid derivative of formula

$$R_{7}$$
 OH (9) or R_{8} OH (10),

in which

R₇ represents hydrogen or C₁-C₄alkyl and

R₈ represents hydrogen or hydroxy or

A₁ and A₂, each one independently of the other, represent a phenol residue of the formula

$$R_{10}$$
 OH (11) or R_{10} OH (12),

in which

 R_9 represents hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, hydroxy, halogen or SO_3H and R_{10} represents hydrogen.

Most preferred compounds of formula (16) are those in which R_1 represents hydrogen or C_1 - C_4 alkoxy, especially hydrogen, R_2 represents SO₃H or CO₂H, especially SO₃H,

 R_3 and R_{3a} both represent hydrogen and the coupling component A_1 is derived from an acetoacetylated amine of formula (2), barbituric acid, cyanoiminobarbituric acid, 2,4,6-triaminopyrimidine, citrazinic acid, a compound of formula (5) or (7) in which R_4 represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen or from salicyclic acid, methyl salicyclic acid, phenol or methyl phenol and the coupling component A_2 is derived from an acetoacetylated amine of formula (2), whereby, in formula (2), X_1 preferably represents methyl and X_2 preferably represents phenyl, which is monosubstituted by SO_3H or, especially, trisubstituted by SO_3H , methyl and methoxy or A_2 is is derived form an aminpyrazole of formula (5) in which R_4

represents C_1 - C_4 alkyl, especially methyl, R_5 represents hydrogen or SO_3H and R_6 represents hydrogen.

Within the scope of the definitions of the above formulae and radicals (1) to (16), a C₁-C₈alkyl radical may be branched or unbranched, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl or 2-ethylhexyl.

Similarly, C₁-C₈alkoxy may be, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy, t-butoxy, 2-ethylbutoxy, n-pentoxy, isopentoxy, 1-methylpentoxy, 1,3-dimethylbutoxy, n-hexyloxy, 1-methylhexyloxy, n-heptyloxy, isoheptyloxy, 1,1,3,3-tetramethylbutoxy. 1-methylheptyloxy, 3-methylheptyloxy, n-octyloxy or 2-ethylhexyloxy

When such alkyl or alkoxy radicals are substituted, appropriate substituents may typically include one or two hydroxy, SO_3H , carboxy, C_1 - C_4 alkoxy, hydoxy-substituted C_1 - C_4 alkoxy, phenyl or phenoxy groups. Suitable radicals of this type may include hydroxyethyl, 1-hydroxyisopropyl, ethoxymethyl, 2-hydroxyethoxypentyl, benzyl, 1-phenylethyl, 2-phenylethyl, 1-isobutyl-3-phenylpropyl or 1-methyl-2-phenoxyethyl.

Halogen in the above formulae and radicals is iodine, bromine, fluorine or, especially, chlorine.

Where, in the derivatives of formulae (4) and (5), R_4 represents C_2 - C_4 alkenyl, this may, for example, be ethenyl, n-propenyl, isopropenyl, n-butenyl or isobutenyl.

Where, in the acetoacetylated amines of formula (2), X₂ represents a 5- or 6-membered heterocyclic ring containing 1-3 heteroatoms and which may be benzannelated, these may be, for example, oxazol-2-yl, thiazol-2-yl, benzoxazol-2-, 5-, or 6-yl, benzothiazol-2-, 5- or 6-yl, benzimidazolone-5-yl, pyrid-2, 3- or 4-yl, quinolin-2-, 4-, 5- or 6-yl or 1,3,5-triazin-2-yl radicals.

The dyes of formula (1) of the invention may be prepared by known methods, for example by tetrazotisation of a diaminobenzanilide derivative of the formula

$$H_2N$$
 H_3
 H_3
 H_2
 H_3
 H_4
 H_2
 H_4
 H_4
 H_5
 H_4
 H_5
 H_5
 H_5
 H_7
 H_8
 H_8

in which R_1 , R_2 , R_3 and R_{3a} are as defined for formula (1), and sequential coupling with a coupling component of the formula A_1H or A_2H , followed by coupling with a coupling component of the formula A_2H or A_1H , A_2 and A_1 being as defined for formula (1).

Such sequential coupling reactions have been described previously (see, for example, US 5,545,725). However, it is advantageous to perform the initial coupling reaction at a pH value of between 2 and 5, especially between 2.5 and 4, whilst the subsequent coupling reaction is performed at a pH value of between 5 and 9, preferably between 6 and 8.

The coupling components A₁H and A₂H are known compounds or may be prepared by known methods, whilst some of the diaminobenzanilides of formula (14) are novel. Consequently, a further aspect of the invention is a compound of the formula

preferably 4,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid or 3,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid, a process for the preparation thereof, by reaction of 2-methoxy-4-nitroaniline-5-sulphonic acid with the appropriate nitrobenzoyl halide, preferably m- or p-nitrobenzoyl chloride, followed by reduction of the resulting dinitrobenzanilide by known methods and also the use of the compound (18) for the preparation of the appropriate compound of formula (1).

The dyes of the invention may be used to dye natural or synthetic materials, for example, cellulosic materials, carbonamide group containing materials such as polyamides, leather or

glass fibres, but are particularly useful for dyeing paper. They are preferably used as a solid or liquid commercial form.

The pulverulent or granular form of the dye is used particularly in batchwise pulp dyeing where the dye mixture, customarily in the form of a stock solution, is added in the pulper, in the beater or in the mixing chest. Preference is here given to using dye preparations which as well as the dye, may further include extenders, for example urea as solubilizer, dextrin, Glauber salt, sodium chloride and also dispersants, dustproofing agents and sequestrants, such as tetrasodium phosphate.

The present invention accordingly further provides solid dye preparations for dyeing paper comprising a compound of the formula (1) and, optionally, further auxiliaries.

In recent years, the use of concentrated aqueous solutions of dyes has gained importance because of the advantages possessed by such solutions when compared with dyes in powder form. The use of solutions avoids the difficulties associated with dust formation and releases the user from the time-consuming and frequently difficult dissolving of the dye powder in water. The use of concentrated solutions was also prompted by the development of continuous dyeing processes for paper, since it is convenient in these processes to meter the solution directly into the pulp stream or to add it at some other suitable point of the paper-making process.

The present invention accordingly further provides aqueous solutions, preferably concentrated solutions, for dyeing paper, comprising a compound of the formula (1), preferably in a concentration of from 5 to 30% by weight. Due to their excellent solubility in water, the dyes of formula (1) are particularly suitable for the preparation of such solutions.

The concentrated solutions preferably contain a low level of inorganic salts, which may be achieved, if necessary, by known methods, for example reverse osmosis.

The solutions may include further auxiliaries, for example solubilizers such as ϵ -caprolactam or urea, organic solvents, for example glycols, polyethylene glycols, dimethyl sulphoxide, N-methylpyrrolidone, acetamide, alkanolamines or polyglycolamines, which is a still further aspect of the invention.

In addition, the aqueous dye solutions of the present invention may be applied to paper by use of the so-called spraying technique.

The novel dyes of the invention dye paper in predominantly yellow shades with excellent degrees of exhaustion with high colour strength, whilst being sufficiently water-soluble to provide stable aqueous formulations without the need for large quantities of solubilizers. Furthermore, dyings obtained exhibit high degrees of bleed- and light-fastness, are even- or top-sided and readily bleachable.

Furthermore, as a result of their high colour strength and water solubility, the novel dyes of the invention are suitable for use in the ink-jet printing method.

Consequently, one further aspect of the invention is paper which is dyed with a compound of the formula (1), either in the form of a solid dye preparation, or an aqueous solution, as described above.

The following Examples serve to illustrate the invention without intending to be restrictive in nature. Parts and percentages are by weight unless otherwise stated.

Synthesis of Intermediate Diaminobenzanilides

Example 1

73.5g of p-penylenediamine 2-sulphonic acid are added to 300g of water and, after addition of approximately 40g of sodium carbonate, the violet suspension is stirred until solution results. The pH is adjusted to 7.5 by addition of concentrated hydrochloric acid and a solution of 78g of p-nitrobenzoyl chloride in 100ml of acetone then added slowly at 25-32°C, the pH being maintained at 6.7-7.0 by addition of 2N aqueous sodium hydroxide. After stirring for a further 1.5 hours, 210ml of water are added and the pH adjusted to 4.0 by addition of 22ml of concentrated hydrochloric acid. The readily stirrable suspension is filtered at room temperature and washed with 200ml of water. The filter cake is then stirred in water at 50°C. filtered hot and dried to yield 75g of 4'amino-4-nitrobenzanilide 3-sulphonic acid. A mixture of 1300g of water, 46.2g of iron filings and 5.8g of ammonium chloride is heated to boiling with vigorous stirring and then treated with 55g of of 4'amino-4-nitrobenzanilide 3sulphonic acid, obtained as described above. The resulting suspension is stirred for a further 1 hour at 95-100°C and, subsequently, cooled to room temperature. The suspension is filtered hot and the filtrate stirred with 5g of Hyflo Carcel™ for 30 minutes at room temperature. After filtering, the pH of the hot filtrate is adjusted to 2.0 by addition of 18g of concentrated hydrochloric acid and the white precipitate filtered and dried. There are obtained 39g of 4,4'diaminobenzanilide 5'-sulphonic acid of formula (100a).

Example 2

74.5g of 2-methoxy-4-nitroaniline 5-sulphonic acid are added to 300g of water and, after addition of approximately 30g of sodium carbonate, the yellowish orange suspension is stirred until solution results. The pH is adjusted to 7.0 by addition of concentrated hydrochloric acid and a solution of 60g of p-nitrobenzoyl chloride in 75ml of acetone then added slowly below 28°C, the pH being maintained at 6.7-7.0 by addition of 2N aqueous sodium hydroxide. After stirring for a further 2 hours, 650g of water are added and the pH adjusted to 4.0 by addition of 2N aqueous hydrochloric acid. The readily stirrable suspension is filtered, the filter cake washed with 200g of water and sucked dry. There are obtained 391g of damp filter cake, which is used directly for the next step.

A mixture of 1000g of water, 60g of iron fillings and 7.6g of ammonium chloride is heated to boiling with vigorous stirring and then treated with 145g of the damp filter cake, obtained as described above. The resulting suspension is stirred for a further 2 hours at 90-95°C and, subsequently, 700g of water are added. The suspension is filtered hot and the filtrate stirred with 10g of Hyflo Supercel™ for 30 minutes at 85°C. After filtering, the pH of the hot filtrate is adjusted to 3.8 by addition of 24g of concentrated hydrochloric acid and the white precipitate filtered and dried. There are obtained 34.3g of 4,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b).

Examples 3-10

By following the procedure described in Examples 1 or 2, employing appropriate starting materials, the following benzanilides may be obtained, as summarized in Table 1 below.

2 0

Table 1

Example Nr.	Compound Nr	. Formula
3	(100c)	H ₂ N SO ₃ H NH ₂
4	(100d)	H ₂ N H ₃ C-O SO ₃ H NH ₂
5	(100e)	H ₂ N—ONH ₂ NH ₂ SO ₃ H
6	(100f)	H ₂ N NH ₂ SO ₃ H
7	(100g)	H ₂ N-OSO ₃ H N-NH ₂ HO ₃ S
8	(100h)	H ₂ N HO ₃ S SO ₃ H NH ₂
9	(100i)	H ₂ N-\Q\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
10	(100j)	H ₂ N CO ₂ H NH ₂

Synthesis of Dyes

Example 11

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with a total of 2.4g of 5-amino-3-methyl-1-(3-sulphophenyl) pyrazole, in portions, at 5°C, the pH being maintained at 3.6-4.0 by addition of a total of 13.7ml of 2N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 70 minutes, to a solution of 1.7g of 5-amino-3-methyl-1-phenyl pyrazole dissolved in 50g of water and 50g of dimethyl formamide, the pH being maintained at 6.5 by addition of a total of 11.9ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1.5 hours at room temperature, 50ml of isopropanol and 30g of sodium chloride are added, the mixture stirred for 1 hour and the resulting yellowish brown suspension filtered. After drying, there are obtained 6.7g of the compound of formula (101).

Example 12

$$CH_3$$
 NH_2
 NH_2
 NH_2
 NH_2
 NH_3
 NH_3
 NH_3
 NH_4
 NH_5
 NH_5
 NH_5
 NH_6
 NH_6
 NH_6
 NH_6
 NH_6
 NH_6
 NH_7
 NH_8
 NH_8

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with 1.75g of 5-amino-3-methyl-1-phenyl pyrazole and reaction continued for 2.5 hours at 5°C, the pH being maintained at 3.8-4.0 by addition of a total of 15.9ml of 2N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 2.5 hours, to a solution of 3.0g of 3-acetoacetylamino-4-methoxy toluene 6-sulphonic acid dissolved in 50g of water and 50g of dimethyl formamide, the pH being maintained at 6.8 by addition of a total of 7ml of 2N aqueous sodium hydroxide solution. After stirring for a further 1.5 hours at 30-35°C, 75ml of isopropanol and 45g of sodium chloride are added and the resulting yellow suspension filtered. After drying, there are obtained 6.8g of the compound of formula (102).

Example 13

$$O = \bigvee_{H=0}^{H=0} \bigvee_{N=0}^{N} \bigvee_{H=0}^{N} \bigvee_{N=0}^{SO_3H} \bigvee_{N=0}^{H_3C} \bigvee_{N=0}^{SO_3H} \bigvee_{N=0}^{N} \bigvee_{N=0}^{N}$$

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is diluted with 60g of water and then treated with 1.2g of barbituric acid. The pH is raised to 2.5 and then maintained at 2.3-2.5 over a period of 3 hours by addition of a total of 5.1ml of 4N aqueous sodium hydroxide solution. The resulting monoazo suspension is then added slowly, during 1.5 hours, to a solution of 3.5g of 3-acetoacetylamino-4-methoxy toluene 6-sulphonic acid dissolved in 100g of water, the pH being maintained at 6.5 by addition of a total of 5.4ml of 4N aqueous sodium hydroxide solution. After stirring for a further 2.5 hours at room temperature, 75ml of isopropanol and 15g of sodium chloride are added and, after stirring briefly at room temperature, the resulting yellowish red suspension is filtered. After drying, there are obtained 7.1g of the compound of formula (103).

Example 14

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is filtered and the moist presscake suspended in 110ml of water. 1.75g of 3-methyl-1-phenyl pyrazo-2-one are added and the pH raised to 3.7. By the addition of a total of 2.5ml of 4N aqueous sodium hydroxide solution, the pH is maintained at 3.5-4.0, whilst the temperature is raised stepwise from 10°C to 30°C. After stirring for a total of 3.5 hours the coupling reaction is complete. To the resulting monoazo suspension are then added 50g of dimethyl formamide followed by 3.5g of 3-acetoacetylamino-4-methoxy toluene

6-sulphonic acid. The pH is adjusted to 7.0-7.5 and maintained at this value by addition of a further 2.7ml of 4N aqueous sodium hydroxide solution. After stirring for a further 2 hours at room temperature, 20g of sodium chloride are added, the mixture stirred for 1 hour at room temperature and the resulting yellow suspension filtered. After drying, there are obtained 5.5g of the compound of formula (104).

Example 15

3.1g of the compound of formula (100a) are suspended in 50g of water and 5.7g of concentrated hydrochloric acid and subsequently treated with 4.75ml of a 4N aqueous sodium nitrite solution at 0-5°C over a period of 1 hour. The mixture is stirred for a further 1 hour and excess nitrite then destroyed by addition of 0.3ml of 2N sulphamic acid. The resultant beige suspension is filtered and the moist presscake suspended in 110ml of water. 1.4g of salicylic acid are added and the pH raised to 3.0-3.3. By the addition of a total of 4.9ml of 2N aqueous sodium hydroxide solution, the pH is maintained at 3.0-3.5. After stirring for a total of 2.5 hours at room temperature the coupling reaction is complete. To the resulting monoazo suspension are then added 3.5g of 3-acetoacetylamino-4-methoxy toluene 6-sulphonic acid. The pH is adjusted to 6.5 and maintained at this value by addition of a further 4.9ml of 2N aqueous sodium hydroxide solution. After stirring for a total of 3.5 hours at room temperature, 10g of sodium chloride and 15ml of isopropanol are added, the pH increased to 8.5 and the resulting yellowish brown suspension filtered. After drying, there are obtained 5.2g of the compound of formula (105).

Examples 16-116

By proceeding in an analogous manner to that described in Examples 11-15, but utilizing the appropriate coupling components, compounds of formula (19) are obtained, as summarized in the following Table 2.

Table 2

Example Nr.	Compound Nr.	A' ₁	A' ₂
16	(106)	н,с н,с-о сн,	н,с то сн,
17	(107)	н,с Тр——— 50,н	H ₃ C-O
18	(108)	H,c N	H ₃ C -O CH ₃ -SO ₃ H
19	(109)	н,с Н д	H ₃ C CH ₃ SO ₃ H
20	(110)	→ H Cu	H ₃ C -O SO ₃ H
21	(111)	H ₂ N NH ₂	н ₃ с — Сн ₃ — So ₃ н
22	(112)	но₂с-√у	H ₃ C -O CH ₃ SO ₃ H

23	(113)	HO ₃ S NH ₂	H ₃ C -O CH ₃ -SO ₃ H
24	(114)	HO ₂ C—OH	н,с-о
25	(115)	CI—OH	н,с н,с-о сн,
26	(116)	CI OH CH ₃	н,с Н,с-о СН,
27	(117)	HO ₃ s————————————————————————————————————	H ₃ C - O SO ₃ H
28	(118)	HO ₃ S CH ₃	H ₃ C O SO ₃ H
29	(119)	HO ₃ S CI OH	н _э с СН _э сн _э - so _э н
30	(120)	HO ₃ S—OH	н,с
31	(121)	OH CO2H	н,с-о
32	(122)	——— СО ₂ Н ———ОН СН ₃	H ₃ C CH ₃ SO ₃ H
33	(123)	но₂с-∕>он	H ₃ C — SO ₃ H
34	(124)	н _а с-	H ₃ C – O CH ₃ – SO ₃ H

	···		
35	(125)	н,с-Сн,	н,с-о
36	(126)	HO ₃ S———OH	H ₃ C SO ₃ H
37	(127)	CH ₃	H ₃ C — SO ₃ H
38	(128)	H ₃ C -O CH ₃	H _s c So _s H
39	(129)	O H O	H ₂ C SO ₂ H
40	(130)	O H CN	H ₂ C SO ₂ H
41	(131)	H ₂ N NH ₂	H ₃ C SO ₃ H
42	(132)	но²с-	H _s c SO ₃ H
43	(133)	HO ₃ S NH ₂	H,C N N N N N N N N N N N N N N N N N N N
44	(134)	NH ₂	н,с Д
45	(135)	OH OH	н,с Д
46	(136)	HO ₂ C-\rightarrow N-\rightarrow CH ₃	н,с Д
47	(137)	CI—()—N—CH,	H,C N SO,H

	· · · · · · · · · · · · · · · · · · ·	T	
48	(138)	CI OH OH	H ₃ C SO ₃ H
49	(139)	HO ₃ S—OH	H,C H
50	(140)	HO ₂ S CI OH	н,с Т
51	(141)	HO ₃ S CI OH	H,c H
52	(142)	HO ₃ S—OH	H,C N-SO,H
53	(143)	OH CO'H	н,с р р го,н
54	(144)	-Со-н	H ₂ C SO ₂ H
55	(145)	−€ CH³	H ₃ C N N N N N N N N N N N N N N N N N N N
56	(146)	но ₂ с-	H,c N N N N N N N N N N N N N N N N N N N
57	(147)	н,с- С-он	н,с Тр—
58	(148)	H ₅ C CH ₅ OH	н,с Тр
59	(149)	но,з-Он	н,с Тр—
60	(150)		н,с р 50,н
61	(151)	H ₃ C-O CH ₃ SO ₃ H	н,с Тр— so,н

	т	T	
62	(152)		н,с Н возн
63	(153)	O H CN	н,с — п— п— п
64	(154)	H ₂ N NH ₂	н,с Тр— зо,н
65	(155)	но с Он	H ₃ C SO ₃ H
66	(156)	HO ₃ S NH ₂	н,с Д
67	(157)	NH ₂	н,с Тр—— so,н
68	(158)	OH CH3	н,с Н — ѕо,н
69	(159)	HO ₂ C-CH ₃	H _s c SO ₃ H
70	(160)	CI—OHNOH	н,с
71	(161)	CI OH CH ₃	н,с Н
72	(162)	HO ₃ S————————————————————————————————————	н,с Н
73	(163)	HO ₃ S CI OH	н,с Н — — — — — — — — — — — — — — — — — —
74	(164)	HO ₃ S CI OH	н,с Д— зо,н
75	(165)	но,ѕ—Он Со,н	н,с — зо,н

76	(166)	OH CO2H	н,с Н — ѕо,н
77	(167)		н,с Д д—
78	(168)	CO ₂ H CH ₃	н,с Н —
79	(169)	но₂с-∕С⊃-Он	н,с Н — — sо,н
80	(170)	н,с-{->-он	н,с Д д
81	(171)	H ₃ C CH ₃ OH	н,с Тр——— so,н
82	(172)	но,ѕ-Ф-он	н,с р- зо,н
83	(173)	−(CH ₃	н"с Н Н — ѕо"н
84	(174)	н,с н,с-о сн,	HO ₃ S NH ₂
85	(175)	н,с Тр— 50,н	HO ₃ S NH ₂
86	(176)	H,C SO,H	HO ₃ S NH ₂
87	(177)	→ H	HO ₃ S NH ₂
88	(178)	→ H ,cn	HO ₃ S NH ₂
89	(179)	H ₂ N NH ₂	HO ₃ S NH ₂

90	(180)	HO ² C—OH	HO ₃ S NH ₂
91	(181)	HO ₃ S—CH ₃	HO _S S NH ₂
92	(182)	HO ₃ S—OH	HO ₃ S NH ₂
93	(183)	OH CO ₂ H	HO ₃ S NH ₂
94	(184)	——Сон	HO ₃ S NH ₂
95	(185)	—————————————————————————————————————	HO ₃ S NH ₂
96	(186)	н,с-{_}он	HO ₃ S NH ₂
97	(187)	но₂с-∕С⊃Он	HO ₃ S NH ₂
98	(188)	————ОН СН ₃	HO ₃ S NH ₂
99	(189)	н,с	⟨ \rightarrow \ri
100	(190)	н,с Н —	⟨ NH₂
101	(191)	H ₂ C N SO ₂ H	NH ₃
102	(192)	HO ₂ C-\rightarrow N CH ₃	√NH ₂ CH ₃
103	(193)	HO,S—CH,	NH ₂

 $\theta = \theta$

104	(194)	OH CO ₂ H	NH ₂
105	(195)	— ОН	NH ₂
106	(196)	—————————————————————————————————————	NH ₂
. 107	(197)	но₄с-∕С	NH ₂
108	(198)	но₃ѕСон	NH ₂
109	(199)	н _з с — сн, н _з с — so _з н	- H
110	(200)	H ₃ C O SO ₃ H	O H CN
111	(201)	H ₃ C-O	H ₂ N NH ₂
112	(202)	H ₃ C — SO ₃ H	но³с—Ди
113	(203)	NH ₂	HO ₃ S NH ₂
114	(204)	NH ₂	H ₃ C SO ₂ H CH ₃
115	(205)	H ₃ C-O	OH CH,
116	(206)	но²с—	H ₃ C -O CH ₃ SO ₃ H

117	(207)	H ₃ C – SO ₃ H	HO ₃ S — O CH ₃
118	(208)	H ₃ C OH CH ₃	н _з с — сн, н _з с – о
119	(209)	H _s C OH CH _s	H ₂ C –O CH ₃ – SO ₂ H
120	(210)	H ₂ NOC O CH ₃	H,C SO,H
121	(211)	н,с о он	H ₃ C –O SO ₃ H
122	(212)	H ₃ C — CH ₃	H²COOH
123	(213)	H ₃ C——OH	H ₂ C OH

Example 124

4.5g of 4,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed

by addition of 0.8ml of 2N aqueous sulphamic acid solution. The resulting yellow suspension is diluted with 60g of water and treated with 2.9g of 5-amino-3-methyl-1-(3-sulphophenyl) pyrazole at 5°C, the pH being initially raised to 3.5 and maintained at 3.0-3-5 by the addition of a total of 27.4ml of 2N aqueous sodium hydroxide solution. After stirring for 2.5 hours the initial coupling reaction is completed. The resulting monoazo suspension is slowly added to a solution of 4.0g of 3-acetacetylamino-4-methoxytoluene 6-sulphonic acid in 50g of dimethylformamide over 2.5 hours at 30°C, the pH being maintained at 6.8-7.0 by addition of a total of 7.3ml of 4N aqueous sodium hydroxide solution. After stirring for 1.5 hours at 30°C, 35g of sodium chloride and 50g of isopropanol are added, the mixture stirred over night and the precipitated solids filtered. After drying, there are obtained 10.2g of the compound of formula (214).

Example 125

$$H_3C-O$$
 H_3C-O
 H

4.5g of 4,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed by addition of 0.8ml of 2N aqueous sulphamic acid solution. The resulting yellow suspension is added to a solution of 7.7g of 3-acetacetylamino-4-methoxytoluene 6-sulphonic acid in 100g of water over 30 minutes at 5°C, the pH being of which is initially adjusted to 3.8 and is maintained at 3.8-4.0 by the addition of a total of 22.6ml of 2N aqueous sodium hydroxide solution. Subsequently, the pH is raised to 6.8-7.4 by addition of a further 10.1ml of 2N aqueous sodium hydroxide solution and the temperature increased to 25-40°C. After stirring

for a total of 3 hours, 45g of potassium chloride and 50g of isopropanol are added and the precipitated solids filtered. After drying, there are obtained 12.9g of the compound of formula (215).

Example 126

2.1g of 4,4'diamino-2'-methoxybenzanilide 5'-sulphonic acid of formula (100b), prepared as described in Example 2, are suspended in 50g of water and 7.6g of concentrated hydrochloric acid and subsequently treated with 5.7ml of 4N aqueous sodium nitrite solution over 1 hour at 0-5°C. The mixture is stirred for a further 1 hour and excess nitrite destroyed by addition of 2N aqueous sulphamic acid solution. The resulting yellow solution is treated with 0.9g of 5-amino-3-methyl-1-phenyl pyrazole at 5°C, the pH being initially raised to 3.0 and maintained at 2.5-3.0 by the addition of a total of 3.1ml of 4N aqueous sodium hydroxide solution. After stirring for 2.5 hours and slowly warming to 20°C, the initial coupling reaction is completed. To the resulting monoazo suspension are added 1.7g of 3-acetacetylamino-4-methoxytoluene 6-sulphonic acid, the pH raised to 6.5 and maintained at 6.0-7.5 by addition of a total of 2.2ml of 4N aqueous sodium hydroxide solution. After stirring for 3 hours at 20-40°C reaction is complete and the precipitated solids are filtered. After drying, there are obtained 5.4g of the compound of formula (216).

Examples 127-198

By proceeding in an analogous manner to that described in Examples 124-126, but utilizing the appropriate coupling components, compounds of formula (20) are obtained, as summarized in the following Table 3.

$$A'_{1} = N_{1}$$

$$N = N_{2}$$

$$H_{2}C = O$$

$$SO_{3}H$$

$$N = N_{1}$$

$$N = A'_{2}$$

$$(20)$$

Table 3

Example Nr.	Compound Nr.	A ' ₁	Λ'.
127	(217)	А' ₁	А'2 H ₃ C — SO,H
128	(218)	H,C SO,H	н,с - о сн,
129	(219)		н,с Н,с-о СН,
130	(220)	→ N CN	н,с н,с-о сн,
131	(221)	H³N NH³	H ₃ C-O CH ₃ SO ₃ H
132	(222)	но-с-	н,с-о
133	(223)	OH OH	н,с-о
134	(224)	HO ₃ S————————————————————————————————————	H ₃ C - O CH ₃ - SO ₃ H
135	(225)	HO ₃ S—OH	н,с-о

 $\mathcal{T}=0$

			
136	(226)	OH CO2H	H ₃ C -O CH ₃ SO ₃ H
137	(227)		H ₃ C — SO ₃ H
138	(228)	CH ₃	н,с-о
139	(229)	ң,с-(он	н,с-о
140	(230)	но _г с-С	H ₃ C — SO ₃ H
141	(231)	€-OH	н,с н,с-о сн,
142	(232)	н,с Тр—С—зо,н	н,с Н — — — 50,н
143	(233)	H,C T N-SO,H	н,с Н————————————————————————————————————
144	(234)	H _s C So ₃ H	н,с Тр—С>-ѕо,н
145	(235)	o H o	н,с Н
146	(236)	N CN	н,с Н-С - so,н
147	(237)	H ₂ N NH ₂	н,с Н
148	(238)	но²с—	н,с Д———— ѕо,н

149	(239)	NH ₂	н,с Тр— sо,н
150	(240)	HO ₃ S NH ₂	н,с Тр—— sо,н
151	(241)	OH CH,	н,с
152	(242)	но,s—СН,	н,с Д——— 50,н
153	(243)	ОН	н,с Д
154	(244)	СС ₂ Н	н,с Тр——— 50,н
155	(245)	н,с-(он	н,с Н — с с с с с с с с с с с с с с с с с
156	(246)	но₄с-∕С—он	н,с —
157	(247)	CH3	н,с Тр—бр-ѕо,н
158	(248)	H ₃ C N N N N N N N N N N N N N N N N N N N	н,с
159	(249)	н,с Тр—— 50,н	н,с
160	(250)	H,C-O	н,с — — — — — — — — — — — — — — — — — — —
161	(251)	, H	H,C THE SO,H
162	(252)	→ H · · · · · · · · · · · · · · · · · ·	н,с разо,н

163	(253)	H ₂ N NH ₂	н,с Д
164	(254)	но³с—Сн	H,c P N SO,H
165	(255)	NH ₂	н,с Н д образован
166	(256)	HO ₃ S NH ₂	H _s c h _s c so ₃ H
167	(257)	OH CH ₃	H,C SO,H
168	(258)	HO ₃ S—OH	H,c H So,H
169	(259)	— Созн	H,c H
170	(260)	—————————————————————————————————————	H,C THE SO,H
171	(261)	н,с-С-Он	H,C N N SO,H
172	(262)	но²с-{-Он	H,C THE SO,H
173	(263)	—————————————————————————————————————	H,C N SO,H
174	(264)	HO ₃ S NH ₂	HO ₃ S NH ₃
175	(265)	H,C N SO,H	HO ₃ S NH ₂
176	(266)	н,с Н————- sо,н	HO ₃ S NH ₂

	·	7	
177	(267)	H ₃ C — SO ₃ H	HO ₃ S NH ₂
178	(268)	- H-o	HO ₃ S NH ₂
179	(269)	O H CN	HO ₃ S NH ₂
180	(270)	H ₂ N NH ₂	HO ₃ S NH ₂
181	(271)	но _в с-	HO ₃ S NH ₂
182	(272)	NH ₂	HO ₃ S NH ₂
183	(273)	OH CH,	HO ₃ S NH ₂
184	(274)	HO ₃ S—OH	HO,S NH ₂
185	(275)	—Сочн	HO ₃ S NH ₂
186	(276)	—————————————————————————————————————	HO ₃ S NH ₂
187	(277)	н,с-(>-он	HO ₃ S NH ₂
188	(278)	но _а с	HO ₃ S NH ₃
189	(279)	CH₃	HO ₃ S NH ₂
190	(280)	ңс Тр—	NH ₃

	·	·	
191	(281)	н,с Тр—— so,н	NH ₂
192	(282)	HO ₃ S NH ₂	NH ₂
193	(283)	HO ₃ S—N—CH ₃	NH ₂
194	(284)	———он	NH ₂
195	(285)	—————————————————————————————————————	NH ₂
196	(286)	н,с-{->-он	NH ₂
197	(287)	но,ѕ	NH ₂
198	(288)	H ₃ C-O	NH ₃

Examples 199-217

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100c) and utilizing the appropriate coupling components, compounds of formula (21) are obtained, as summarized in the following Table 4.

$$N=N$$

$$N=N$$

$$N=N$$

$$N=N$$

$$N-A'_{2}$$

$$N-A'_{2}$$

Table 4

Evample Mr	Compound Nr	Α'	Α,
Example Nr.	Compound Nr.	A' ₁	A' ₂
199	(289)	H ₃ C N SO ₃ H	H ₃ C SO ₃ H
200	(290)	н,с Нр——— so,н	н _з с Сн ₃
201	(291)	H ₃ C H	H ₃ C — SO ₃ H
202	(292)		н,с н,с-о сн,
203	(293)	CN CN CN	H ₃ C –O CH ₃ —SO ₃ H
204	(294)	H ₂ N NH ₂	H ₃ C CH ₃ SO ₃ H
205	(295)	но³с—	H ₃ C-O CH ₃ SO ₃ H
206	(296)	HO ₃ S NH ₃	H ₂ C-OCH ₃
207	(297)	CH _a	н,с-о
208	(298)	OH NHOH,	H ₃ C-O
209	(299)	HO ₃ S—OH	н,с — Н,с-о Сн,

210	(300)		H ₃ C O CH ₃
211	(301)	CH ₂	H ₃ C O CH ₃ SO ₃ H
212	(302)	н,с-С-	H ₃ C O CH ₃ N SO ₃ H
213	(303)	но₂с-∕С	н,с Н,с-о сн,
214	(304)	{Сн _а	H ₃ C CH ₃ CH ₃ SO ₃ H
215	(305)	HO ₃ S NH ₂	NH ₂
216	(306)	HO ₃ S NH ₂	HO ₃ S NH ₂
217	(307)	NH ₂	HO ₃ S NH ₂

Examples 218-236

By proceeding in an analogous manner to that described in Examples 124-126, but replacing the compound of formula (100b) by the compound of formula (100d) and utilizing the appropriate coupling components, compounds of formula (22) are obtained, as summarized in the following Table 5.

$$N=N$$

$$H_3C-O$$

$$SO_3H$$

$$N-A'_2$$

$$N-A'_2$$

Table 5

Example Nr.	Compound Nr.	A' ₁	A' ₂
218	(308)	H ₃ C -O SO ₃ H	H ₃ C SO ₃ H
219	(309)	н,с Д д	H ₃ C-O
220	(310)	н,с Д	н ₃ с-о
221	(311)		н,с-о
222	(312)	O H CN	н,с н,с-о
223	(313)	H ₂ N NH ₂	H,C-O CH, SO,H
224	(314)	HO ₂ C—OH	H ₃ C-O CH ₃ SO ₃ H
225	(315)	HO ₃ S NH ₂	H ₃ C CH ₃ SO ₃ H
226	(316)	NH ₂	H ₃ C — SO ₃ H
227	(317)	OH CH,	н,с сн, со, н
228	(318)	HO ₃ S—OH	н,с-о

229	(319)	-Созн	H ₃ C — SO ₃ H
230	(320)	CO ₂ H CH _s	н ₃ с — сн, - so ₃ н
231	(321)	н _э с—Сон	H ₃ C –O CH ₃ –SO ₃ H
232	(322)	но₂с-∕С⊃-он	н,с-о
233	(323)	CH,	н,с н,с-о сн,
234	(324)	HO ₃ S NH ₂	NH ₂
235	(325)	HO ₃ S NH ₂	HO ₃ S NH ₂
236	(326)	NH ₂	HO ₃ S NH ₂

Examples 237-255

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100e) and utilizing the appropriate coupling components, compounds of formula (23) are obtained, as summarized in the following Table 6.

$$A'_{1} = N$$

$$N = N$$

$$N = N$$

$$A'_{2}$$

$$(23)$$

Table 6

Example Nr.	Compound Nr.	A' ₁	A'2
237	(327)	н,с-о	H ₃ C-O CH ₃ SO ₃ H
238	(328)	н,с Др——— so,н	н,с-о
239	(329)	н,с Д (H ₃ C-O CH ₃ CH ₃ SO ₃ H
240	(330)		H ₃ C-O
241	(331)	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	H ₃ C-O CH ₃ SO ₃ H
242	(332)	H ₂ N NH ₂	H ₃ C-O
243	(333)	HO ³ C— OH	H,C-O
244	(334)	HO ₃ S NH ₂	H ₃ C – SO ₃ H
245	(335)	NH ₃	H ₃ C -O CH ₃ SO ₃ H
246	(336)	OH CH,	H ₃ C-O CH ₃ SO ₃ H
247	(337)	HO ₃ S————————————————————————————————————	н,с - о сн,

248	(338)		н _з с-о
249	(339)	—————————————————————————————————————	н,с-о
250	(340)	н,с-{}-он	н,с - о сн,
251	(341)	но₃с-∕С}-он	н,с н,с-о
252	(342)	———OH CH₃	н,с-о
253	(343)	HO ₃ S NH ₂	NH ₂
254	(344)	HO ₃ S NH ₂	HO ₃ S NH ₂
255	(345)	NH ₂	HO ₃ S NH ₃

Examples 256-274

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100f) and utilizing the appropriate coupling components, compounds of formula (24) are obtained, as summarized in the following Table 7.

$$\begin{array}{c}
A'_1 \\
N=N
\end{array}$$

$$\begin{array}{c}
O \\
N=N
\end{array}$$

$$A'_2$$

$$A'_2$$

$$A'_3$$

Table 7

Example Nr.	Compound Nr.	A ' ₁	A'2
256	(346)	H,C-O	н ₃ с — сн ₃ — so ₃ н
257	(347)	н,с Тр—— ѕо,н	H ₃ C O SO ₃ H
258	(348)	H _a C SO ₂ H	H ₃ C CH ₃ CH ₃ So ₃ H
259	(349)		H ₃ C –O CH ₃ – SO ₃ H
260	(350)	- H v,cn	H ₃ C CH ₃ SO ₃ H
261	(351)	H ₂ N NH ₂ NH ₂ N	H ₃ C O SO ₃ H
262	(352)	но,с-	H ₃ C — SO ₃ H
263	(353)	HO ₃ S NH ₂	н,с-о

264	(354)	NH ₂	н,с н,с-о сн,
265	(355)	OH CH ₃	H ₃ C -O CH ₃ -SO ₃ H
266	(356)	HO ₃ S—OH	н,с н,с-о сн,
267	(357)	———он	н _у с — сн, н _у с — so, _у н
268	(358)	—————————————————————————————————————	H ₃ C — SO ₃ H
269	(359)	н,с-Ф-он	н,с-о
270	(360)	но³с-{	н,с н,с-о сн,
271	(361)	→ OH CH ₃	H ₃ C – SO ₃ H
272	(362)	HO ₃ S NH ₃	NH ₂
273	(363)	HO ₃ S NH ₂	HO ₃ S NH ₃
274	(364)	NH ₂	HO ₃ S NH ₂

Examples 275-286

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100g) and utilizing the

appropriate coupling components, compounds of formula (25) are obtained, as summarized in the following Table 8.

Table 8

Example Nr.	Compound Nr.	A' ₁	A' ₂
275	(365)	NH ₂	н,с н,с-о сн,
276	(366)	NH ₃	н,с р
277	(367)	NH ₂	н,с д зо,н
278	(368)		NH ₂
279	(369)	O CN	NH ₂
280	(370)	H ₂ N NH ₂	NH ₂
281	(371)	HO³C——OH	NH ₂
282	(372)	-Со³н	NH ₂

283	(373)	—————————————————————————————————————	NH ₂
284	(374)	ңс-С-он	NH ₂
285	(375)	но₂с—∕Он	NH ₂
286	(376)	СН,	NH ₂

Examples 287-298

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100h) and utilizing the appropriate coupling components, compounds of formula (26) are obtained, as summarized in the following Table 9.

$$N=N$$

$$N=N$$

$$HO_3S$$

$$N-A'_2$$

$$N-A'_2$$

$$N-A'_2$$

Table 9

Example Nr.	Compound Nr.	A' ₁	A' ₂
287	(377)	NH ₂	H ₃ C CH ₃ SO ₃ H
288	(378)	NH ₂	н,с Н — \$0,4
289	(379)	NH ₂	н,с Тр—

290	(380)		NH ₂
291	(381)	O H CN	NH ₂
292	(382)	H ₂ N NH ₂	NH ₂
293	(383)	HO ₂ C—OH	NH ₂
294	(384)	———он	NH ₂
295	(385)	————он Сн _з	NH ₂
296	(386)	н,с-(он	NH ₂
297	(387)	но₂с-∕С—он	NH ₂
298	(388)	—————————————————————————————————————	NH ₂

Examples 299-365

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100i) and utilizing the appropriate coupling components, compounds of formula (27) are obtained, as summarized in the following Table 10.

$$A'_{1} = N$$

$$N = \begin{pmatrix} O & CO_{2}H \\ N & N - A'_{2} \end{pmatrix}$$

$$(27)$$

Table 10

Example Nr.	Compound Nr.	A' ₁	A' ₂
299	(389)	н,с Д — 50,н	н,с н,с-о сн,
300	(390)	H ₃ C N N N N N N N N N N N N N N N N N N N	H ₃ C – SO ₃ H
301	(391)		H,C CH, H,C-O CH, SO ₃ H
302	(392)	- H CN	H,C SO,H
303	(393)	H ₂ N NH ₂	H ₃ C-O CH ₃ SO ₃ H
304	(394)	HO³C————————————————————————————————————	H ₃ C-O CH ₃ SO ₃ H
305	(395)	OH CH,	H ₃ C-O CH ₃ SO ₃ H
306	(396)	HO ₃ S—OH	H,C — SO,H
307	(397)	HO ₃ S OH	н,с-о сн,
308	(398)	OH CO₂H	H ₃ C-O
309	(399)	—————————————————————————————————————	H ₃ C — SO ₃ H

			
310	(340)	н,сСон	н,с о о о сн,
311	(401)	но₂с-∕С}—он	H ₃ C-O CH ₃ SO ₃ H
312	(402)	———ОН СН _а	H ₃ C CH ₃ SO ₃ H
313	(403)	н,с	H ₂ C H_SO ₂ H
314	(404)	H,C THE SO,H	н,с — —
315	(405)	H ₃ C – SO ₃ H	н,с Н
316	(406)		H ₃ C N—So ₃ H
317	(407)	→ H v cn	н,с — — —
318	(408)	H ₂ N NH ₂	н,с Н
319	(409)	но с Он	н,с Н — 50,н
320	(410)	NH ₃	н,с
321	(411)	HO ₃ S NH ₂	н,с Н — 50,н
322	(412)	OH CH,	н,с Н————————————————————————————————————
323	(413)	HO ₃ S—OH	н,с Н

324	(414)	—————————————————————————————————————	н,с Др—— ѕо,н
325	(415)	н _з с-{_>он	н,с Д———— 50,н
326	(416)	но₃с-∕С—он	н,с Ч
327	(417)	→CH ₃	н,с Др-С
328	(418)	H,c H SO,H	н,с Д———— sо,н
329	(419)	н,с Тр—С>—so,н	н,с Тр—С>-ѕо,н
330	(420)	н,с н,с-о сн,	н,с Тр——— sо,н
331	(421)		H _s c N So ₃ H
332	(422)	O H CN	H,C P N-SO,H
333	(423)	H ₂ N NH ₂	H _s c h
334	(424)	но,с-	H,C N SO,H
335	(425)	NH ₂	H,c N N N N N N N N N N N N N N N N N N N
336	(426)	HO ₃ S NH ₃	H,C SO,H
337	(427)	OH CH,	н,с Н

338	(428)	HO ₃ S—OH	H ₂ C SO ₂ H
339	(429)	—————————————————————————————————————	H,C H
340	(430)	н,с	H,C H
341	(431)	но₂с—∕Он	H ₃ C SO ₃ H
342	(432)	—————————————————————————————————————	н,с Тр
343	(433)	HO ₃ S NH ₂	HO ₃ S NH ₂
344	(434)	н,с Д	HO ₃ S NH ₂
345	(435)	н,с п со во	HO ₃ S NH ₂
346	(436)	H ₃ C O SO ₃ H	HO ₃ S NH ₂
347	(437)		HO ₃ S NH ₂
348	(438)	→ H CN	HO ₃ S NH ₂
349	(439)	H ₂ N NH ₂	HO ₃ S NH ₂
350	(440)	но₁с— Он	HO ₃ S NH ₂
351	(441)	NH ₃	HO ₃ S NH ₂

352	(442)	OH CH,	HO ₃ S NH ₂
353	(443)	HO ₃ S—OH	HO ₃ S NH ₂
354	(444)		HO ₃ S NH ₂ CH ₃
355	(445)	н,сС-он	HO ₉ S NH ₂
356	(446)	но₂с-∕С—он	HO ₃ S NH ₂
357	(447)	-Сн,	HO ₃ S NH ₂
358	(448)	H ₃ C The so,H	NH ₂
359	(449)	н,с Тр——50,н	NH ₂
360	(450)	HO ₃ S NH ₂	NH ₂
361	(451)	HO ₃ S—OH	NH ₂
362	(452)	Содн	NH ₂
363	(453)	—————————————————————————————————————	NH ₂
364	(454)	но²с-∕С-Он	NH ₃
365	(455)	но _з ѕ	NH ₂

Examples 366-436

By proceeding in an analogous manner to that described in Examples 11-15, but replacing the compound of formula (100a) by the compound of formula (100J) and utilizing the appropriate coupling components, compounds of formula (28) are obtained, as summarized in the following Table 11.

$$N=N$$

$$N=N$$

$$N=N$$

$$N-A'_{2}$$

$$N-A'_{2}$$

$$N=N$$

$$N-A'_{2}$$

Table 11

Example Nr.	Compound Nr.	A' ₁	A'2
366	(456)	н,с — — — — — — — — — — — — — — — — — — —	H ₃ C-O CH ₃ SO ₃ H
367	(457)	н,с Тр-	н,с н,с-о сн,
368	(458)		н,с н,с-о сн,
369	(459)	→ H CM	н,с — — — — — — — — — — — — — — — — — — —
370	(460)	H ₂ N NH ₂	н,с н,с-о сн,
371	(461)	но _г с	н,с-о

372	(462)	OH CH,	н ₃ с — Н ₃ с — SO ₃ H
373	(463)	HO ₃ S————————————————————————————————————	H ₃ C - SO ₃ H
374	(464)	HO ₂ S———N—CO ₂ H	H ₃ C CH ₃ CH ₃ So ₃ H
375	(465)	OH CO ₂ H	H ₃ C-O CH ₃ SO ₃ H
376	(466)	———он	H ₃ C — SO ₃ H
377	(467)	————OH CH₃	H ₃ C-O CH ₃ SO ₃ H
378	(468)	н,сСон	H ₃ C-O CH ₃ SO ₃ H
379	(469)	но _э с-С	H,C-O
380	(470)	———OH CH₃	H ₃ C CH ₃ SO ₃ H
381	(471)	н,с Тр—С>-ѕо,н	н,с Н
382	(472)	H,C N N SO,H	н,с — п—— so,н
383	(473)	н,с Н,с-о сн,	н,с Н
384	(474)	- Ph	н,с Н — — - 50,н

385	(475)	O H N.CN	н,с Н
386	(476)	H ₂ N NH ₂	н,с Н
387	(477)	но₂с— Он	н,с Н р— so,н
388	(478)	NH ₂	н,с Д———— so,н
389	(479)	HO ² S, NH ³	н,с Тр—С>-ѕо,н
390	(480)	OH CH3	H ₃ C N————————————————————————————————————
391	(481)	HO ₃ S—N—CH ₃	H ₃ C H SO ₃ H
392	(482)	— ОН	н,с Н — 50,н
393	(483)	—————————————————————————————————————	н,с Н н-С - so,н
394	(484)	н,с	H ₃ C SO ₃ H
395	(485)	но₃с-∕С>-он	н,с Тр——— 50,н
396	(486)	Сн,	н,с Тр—Сэо,н
397	(487)	н,с П	н,с Н 50,н
398	(488)	н,с Тр—— so,н	н,с Тр—— so,н

399	(489)	н,с-о	н,с Тр— ѕо,н
400	(490)	→ H=o	н,с р р годн
401	(491)	→ H · · · · · · · · · · · · · · · · · ·	н,с Др-
402	(492)	H ₂ N NH ₂	н,с Н д 50,н
403	(493)	но с он	H,c H
404	(494)	NH ₂	H,c So,H
405	(495)	HO ₃ S NH ₂	H,C T SO,H
406	(496)	OH CH ₃	H ₂ C SO ₃ H
407	(497)	HO ₃ S—OH	н,с Н В В В В В В В В В В В В В В В В В В
408	(498)	—————————————————————————————————————	н,с
409	(499)	—————————————————————————————————————	H,C The So,H
410	(500)	н,с-С-он	н,с Тр
411	(501)	но _з с-Д-он	н,с П
412	(502)	—————————————————————————————————————	н,с Тр-

413	(503)	HO ₃ S NH ₂	HO ₃ S NH ₂
414	(504)	н,с Д	HO ₃ S NH ₂
415	(505)	н,с Тр—Сэо,н	HO ₃ S NH ₂
416	(506)	н _э с — сн, н _э с — so _э н	HO ₃ S NH ₂
417	(507)		HO ₃ S NH ₂
418	(508)	O H CN	HO ₃ S NH ₂
419	(509)	H ₂ N NH ₂	HO ₃ S NH ₂
420	(510)	но с он	HO ₃ S NH ₂
421	(511)	NH ₂	HO ₃ S NH ₂
422	(512)	OH CH,	HO ₃ S NH ₂
423	(513)	HO ₃ S—OH	HO ₃ S NH ₂
424	(514)	———ОН ———ОН	HO ₃ S NH ₂
425	(515)	—————————————————————————————————————	HO ₃ S NH ₂
426	(516)	н,с-(он	HO ₃ S NH ₂

427	(517)	но₂с-∕С—он	HO ₃ S NH ₃
428	(518)	CH ₃	HO ₃ S' NH ₂
429	(519)	H ₃ C N SO ₃ H	NH ₂
430	(520)	н,с ү ү	NH ₂
431	(521)	HO ₃ S NH ₂	NH ₂
432	(522)	HO ₃ S—OH	NH ₂
433	(523)	———он	NH ₂
434	(524)	————он сн,	NH ₂
435	(525)	но₂с-∕>он	NH ₂
436	(526)	но₃ѕСон	NH ₃

Application Examples

Example 437 - Unsized without filler

A mixture consisting of 50% long fibre spruce sulphite bleached and 50% short fibre beech sulphite bleached fibres is suspended in deionised water, as a 2% suspension, and refined and beaten to 22°SR (Schopper Riegler). After dewatering by means of a centrifuge and testing for dry weight, the equivalent to 10g of dry fibre are placed in a beaker and made up to a volume of 500ml with tap water. After stirring for 1 hour, 0.42%, based on the weight of dry fibre, of compound (101) as a 5g/l aqueous solution are added to the furnish suspension

and stirring continued for a further 15 minutes. The suspension is made up to 700ml with water and from 300ml of the resulting suspension a hand sheet is produced using a Lhomargy sheet former. After drying on a cylinder at 90°C for 12 minutes, a greenish-yellow dyeing is obtained showing excellent bleed-fastness to water, soda and acetic acid and good light-fastness. The backwater from the dyeing is almost colourless and the degree of exhaustion amounts to 92-94%.

Examples 438-

The procedure described in Example 437 is repeated using, instead of compound (101), sufficient amounties of the appropriate dye to produce a dyeing of standard depth 0.2. The degrees of exhaustion of the respective dyes are calculated and the results summarized in Table 12 below.

Table 12

Example Nr.	Compound Nr.	Degree of Exhaustion in %
438	(102)	98
439	(103)	98
440	(104)	92-94
441	(105)	98-99
442	(106)	93-94
443	(107)	93
444	(108)	92
445	(110)	98
446	(135)	97-98
447	(151)	95
448	(157)	98-99
449	(189)	95
450	(190)	97.5
451	(200)	96.5
452	(205)	97
453	(214)	95-97

453	(216)	97-98
454	(267)	93
455	(288)	98

The above results clearly demonstrate the excellent degrees of exhaustion of the dyes tested, the backwater, in all cases, being almost colourless.

Example 456 - Neutral sized with filler

A mixture consisting of 50% long fibre spruce sulphite bleached and 50% short fibre beech sulphite bleached fibres is suspended in deionised water, as a 2% suspension, and refined and beaten to 35°SR (Schopper Riegler). After dewatering by means of a centrifuge and testing for dry weight, the equivalent to 10g of dry fibre and 2g of dry chalk filler are placed in a beaker and made up to a volume of 500ml with tap water. After stirring for 1 hour, 0.78%, based on the weight of dry fibre, of compound (101) as a 5g/l aqueous solution are added to the furnish suspension and stirring continued for a further 15 minutes. 2% of alkyl ketene dimer size is then added, the suspension stirred for 30 minutes, 0.05% retention aid added and the suspension stirred vigorously for a further 5 minutes. The suspension is made up to 700ml with water and from 300ml of the resulting suspension a hand sheet is produced using a Lhomargy sheet former. After drying on a cylinder at 90°C for 12 minutes, a greenish-yellow dyeing is obtained showing excellent fastness values. The backwater from the dyeing is only weakly coloured.